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METHOD FOR GASIFYING ORGANIC SUBSTANCES AND SUBSTANCE MIXTURES

AND APPARATUS

A The invention relates to a method for gasifying organic substances and substance mixtures ~~according to the generic terms of Claim 1~~.

A INS A2 A1 BACKGROUND OF THE INVENTION

From US-PS 4,568,362, a method for gasifying organic substances and substance mixtures is known in which the organic substances are directed into a pyrolysis reactor in which the organic substances come into contact with a heat carrier medium which causes rapid pyrolysis in which the organic substances are converted into pyrolysis products, that is, pyrolysis gases with substances that can be condensed and solid residue containing carbon. The heat energy needed for the pyrolysis is generated by firing the solid residue containing carbon. In a second reaction zone, the pyrolysis gases that contain tar are subjected to cracking reactions and reactions with steam such that a product gas with a high caloric value is obtained.

In this method, the pyrolysis as well as the firing of the solid residue containing carbon take place in a fluidized bed. In the upper part of the pyrolysis fluidized bed reactor, a reaction zone is provided for the pyrolysis gases containing tar.

The heat carrier medium is discharged together with the solid residue containing carbon in part through the reactor head of the pyrolysis fluidized

bed reactor and the remaining portion via a line that is mounted on the upper fluidized bed limit, and fed to the fluidized bed firing. There, the solid residue containing carbon is fired and the heat carrier medium heated up. The heated heat carrier medium and the ashes are discharged from the fluidized bed firing together with the waste gas, and separated in a gas-solid separator mounted above the fluidized bed pyrolysis reactor, and fed to the reaction zone of the pyrolysis reactor from which it again falls into the fluidized bed of the pyrolysis reactor (heat carrier medium cycle).

It is very costly to operate the fluidized beds and it is hardly possible to control the reactions of the pyrolysis gases in the reaction zone.

INS A3 > ~~The object of the invention is to make available~~ a method AND AN APPARATUS for generating a gas with a high caloric value that is easy to ~~perform. In this process,~~ PERFORM AND RESULTS IN a small condensation portion ~~is preferred. A further object of the invention is to make available a simple apparatus for carrying out the method~~.

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SUMMARY OF THE INVENTION

INS A4 > ~~With respect to the method, this object is resolved by the combination of features in Claim 1.~~ According to the invention, the pyrolysis is carried out in a fluidized bed reactor or a rotary drum, the pyrolysis gases are mixed, if necessary, with a reactant such as steam, and they are fed into an indirect heat exchanger in which the pyrolysis gases react with the reactant. The solid residue containing carbon and the heat exchanger medium are fed to a firing. The firing waste gases are fed through the indirect heat exchanger such that their heat content is used for the reaction of the pyrolysis gases with the reactant. The ashes of the solid residue containing carbon and the heat carrier medium taken from the firing are fed into the pyrolysis reactor at the entry end for the organic substance.

The invention involves the basic concept that gasifying methods should be divided into three method steps that can be carried out easily. In a first method step, pyrolysis of the substances used takes place rapidly. In the process, the goal is to have as little as possible of the condensable substances in the pyrolysis gases. The rapid pyrolysis is ensured by performing the pyrolysis of the substances used at a temperature of 550-650°C.

In a second method step, the pyrolysis gases are heated and reacted with steam to adjust the product gas quality. The reaction of the pyrolysis gases is carried out with steam at a temperature of 900-1000°C.

In a third method step, the solid pyrolysis residue containing carbon is fired. The heat generated in the process is used for the pyrolysis and the reaction of the pyrolysis gases. Furthermore, the heat carrier medium is heated up in the firing and then is conveyed back into the pyrolysis reactor. The heat transfer for the reaction of the pyrolysis gases with steam takes place in a heat exchanger that is heated by the waste gases from the firing.

The advantage of this division of the three method steps is that each method step and the combination of the method steps can be arranged according to the set standard of gas product quality.

The set standard for the gas product quality is first of all, a higher caloric value. Furthermore, the steam content is increased by the second method step so that the gas product is very well suited for use as a synthesis gas, and energy use in connection with fuel cells can also be considered. Naturally, use to obtain energy via a gas motor or gas turbine is also possible.

The reactant is steam. It is possible to avoid the addition of steam when sufficient water vapor is contained in the feedstock used, for example, when the material used is not dried or only to a limited extent. Furthermore, it is possible that the pyrolysis gases that form contain sufficient water vapor when sufficient steam develops in the pyrolysis of the substances used. It is also possible to provide the addition of steam in the pyrolysis step.

With the method according to the invention, basically all organic substances and substance mixtures can be gasified. However, it is preferable to gasify biomasses.

The substances used must be pretreated before they are fed to the pyrolysis. The pretreatment is generally limited to drying and if necessary, to pulverization. In the process, no great restrictions are set for the lumpiness of the substances used because the pyrolysis is carried out in a fluidized bed with a heat carrier medium.

To improve the cracking of the noncondensable substances in the pyrolysis gas, a catalyst can be provided in the reaction of the pyrolysis gases with steam. Preferred catalysts are dolomite, calcite, nickel, nickel oxide, nickel aluminate, or nickel spinel.

When dolomite is used, it is advantageous to calcinate the dolomite at the reaction temperature of 900-1000°C, and the resulting calcium/magnesium oxide has particularly high catalytic activity.

The reaction temperature of 900-1000°C is advantageous for the reaction of the pyrolysis gas with steam, because in this temperature range, the sulfur sensitivity of the named catalysts is very much reduced. There is the possibility of regenerating the catalysts from time to time in situ by the addition of a small amount of air at temperatures above 1000°C.

The catalysts can also be used as a heat carrier medium. This manner of proceeding has the advantage that the catalysts are periodically regenerated in the heat carrier cycle.

To prevent the catalyst from being deactivated by dust, it is recommended that the hot pyrolysis gases be dedusted before addition of the steam.

In cases in which, because of the substances used, there is only minimal development of pyrolysis coke and thus the heat developing in the firing is not sufficient for pyrolysis and reaction with steam, a portion of the pyrolysis gas can be fired to generate heat.

The firing of a portion of the pyrolysis gas to generate heat is also required when the pyrolysis coke is used as a material, for example, for the production of activated charcoal or grilling charcoal or charcoal briquettes. So that the pyrolysis coke can be transferred out well, the grain size of the heat carrier medium must be small enough that the heat carrier medium can be separated from the pyrolysis coke without any problem.

For the device according to the invention, simple and cost-effective components can be used that are known as such and easily available. With these components, the device according to the invention can easily be constructed.

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The pyrolysis takes place in a moving bed reactor using a heat carrier medium. A shaft kiln is primarily used for this into which the mixture consisting of the material to be gasified and the heat carrier medium is loaded from above. The mixture travels through the shaft kiln. Rapid pyrolysis occurs due to the intimate contact of the material used with the heat carrier medium.

So that even with heterogeneous materials, transport through the shaft kiln is ensured, built-in structures or spiral conveyors can be provided inside the shaft kiln. The built-in structures also have the advantage that the pyrolysis gases developing can better escape upwards through the moving bed. Nevertheless, the equipment expense is increased in this way.

Basically, the pyrolysis can also be carried out in a rotary drum or a double-deck oven, although here as well, the equipment cost would be greater.

The mixture consisting of the heat carrier medium and the pyrolysis residue can be transferred into the firing via commercially available aggregates such as conveyor worms, swivel grates, rotating grates or cellular wheel sluices. In combination with a grate firing, however, the use of feeding rams is preferred. When an underfeed stoker is used, the use of conveyor worms is preferred. The firing waste gases are fed through an indirect heat exchanger that simultaneously serves as chemical reactor in which the pyrolysis gases react with steam. Such heat exchangers are known, for example, in refineries as steam reformers or reformers.

Also for the conveyance of the heat carrier medium from the firing into the shaft kiln, conventional conveyance devices can be used, such as vibrating conveyors, bucket conveyors, or chain conveyors. The demands on conveyance technique also correspond to the requirements that appear in the steel industry or in the field of coking, so that excessive expense is not required for layout of the aggregates.

The heat carrier medium must have sufficient mechanical, chemical, and thermal stability in the temperature range of 600-1000°C. Fire-resistant substances such as sand, silicon, grit, aluminum silicates, corundum, graywacke, quartzite, or cordierite are used. The use of molded bodies of metallic or non-

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metallic materials or combinations of them, such as steel or ceramic balls is also possible.

With respect to the particle size, the heat carrier medium must be fine enough to be able to make intimate contact with the material used so that a good transfer of heat can take place. On the other hand, the particles of the heat carrier medium must be big enough that there is sufficient empty volume through which the pyrolysis gases can flow.

These requirements are best fulfilled when the heat carrier medium has a grain size of 1-40 mm. This grain size also has the advantage that the heat carrier medium can be separated well from the ash of the pyrolysis residue after the firing.

As mentioned above, a catalyst can be provided for the reaction of the pyrolysis gases with steam. For this purpose, a catalyst bed can be mounted in the heat exchanger. Depending on whether the pyrolysis gases are fed through the pipes of the heat exchanger or outside the pipes through heat exchanger, the catalyst bed is mounted inside or outside of the pipes of the heat exchanger. It is also possible to use a catalytically active material for the heat exchanger pipes such as corundum with nickel or nickel oxide. It is also possible to provide a solid bed reactor with a catalyst bed behind the heat exchanger.

If the reaction of the pyrolysis gases with steam is to be supported by a catalyst, it is recommended that the hot pyrolysis gases be dedusted with a filter before contact with the catalyst.

The method steps named above as well as those claimed and described in the embodiment example, which are to be used according to the invention, as well as structural components are not subject to any special exceptional restrictions with respect to their method restrictions, their size, shape, material selection, and technical conception, so that the selection criteria known in the particular area of application in each case can be used without any limitations.

INS A5

~~Further details, features, and advantages of the object of the invention result from the following description of the related illustration in which, as an~~

INS A6 ~~example, a preferred embodiment of the gasifying of organic materials is repre-sented. Shown in the illustration are~~:

Figure 1, a diagram of the method according to the invention,

Figure 2, the mass and energy balance of the pyrolysis and reaction steps,

Figure 3, the mass and energy balance of the firing, and

Figure 4, a schematic representation of a device for carrying out the method according to the invention.

A DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

INS A7 ~~It is evident from Figure 1~~ that the material to be gasified 1 is fed into pretreatment step 2. Depending on the material, this can be a drying and/or pulverization device in which the material is prepared for the subsequent pyrolysis. The pretreated material 1 is brought into pyrolysis step 3. The pyrolysis step 3 leaves a pyrolysis gas 5 and a pyrolysis coke 5a.

The pyrolysis coke 5a is fired in firing 6. The heat from firing 6 is directed via a heat coupling 7 to pyrolysis step 3 and via a heat coupling 7a to a reaction zone 4 for pyrolysis gas. The waste gases 18 of firing 6 are cooled and diverted in a flue gas cleaning and cooling step 17. The waste heat obtained with the flue gas cleaning and cooling step 17 can be used, for example, for the drying in pretreatment step 2.

Depending on the method conditions, more heat may develop in firing 6 than is needed for heat coupling 7 and 7a. Steam can be generated with this heat. For this, feed water 9 can be fed via water treatment 10 and pump 11 into heat exchanger 12 which is mounted in firing 6. The steam 16 generated is fed into reaction zone 4. The pressure of the unneeded portion can be released via turbine 13 and further utilized as waste steam 16a.

The pyrolysis gas 5 is fed into reaction zone 4 with steam 16. In this reaction zone, the pyrolysis gas and the crack products of the condensable substances are reacted with steam to the desired gas product 15. The gas product 15 is then purified in a dedusting 8 and fine dedusting and quenching 14. It is also possible to feed a portion 19 of the gas product 15 into pyrolysis 3.

The addition of air and/or oxygen can be provided in the individual

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method steps to influence the method steps of pyrolysis, firing, and reaction with steam. B1

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A ~~Figure~~ FIGURE 2 shows the mass and energy balance of a pyrolysis step 101 and a reaction step 102 in the example of gasifying wood. Wood 104 and heat carrier medium 104a are introduced into pyrolysis step 101. Furthermore, heat flow 111a, that results from the size and consistency of the material flows consisting of wood 104 and heat carrier medium 104a, as well as the targeted pyrolysis temperature, is added. Pyrolysis step 101 leaves a mixture 105 consisting of wood charcoal and heat carrier medium, and pyrolysis gas 106.

INS B2

Pyrolysis gas 106 enters reaction step 102. Furthermore, a heat loss 108 occurs. Additionally, the reaction heat of the wood charcoal formation 109 and steam 112 are fed into reaction step 102. In addition, another heat loss 110 occurs. Resulting from the heat and material streams fed in and diverted out, is still the heat quantity 111 to be fed in.

A In ~~Figure~~ FIGURE 3, the mass and energy balance of the wood charcoal firing 103 is represented. The material streams, mixture 105 (consisting of wood charcoal and heat carrier medium 104a), water 117, and air 113 enter into the firing, and also the material streams, waste gas 116, steam 112, and mixture 118 (consisting of heat carrier medium 104a and ash), exit. Heat streams that appear are heat stream 111 that is fed into reaction step 102, heat stream 111a that is fed into pyrolysis step 101, heat excess 114, and heat loss 115.

A ~~Figure~~ FIGURE 4 shows a device for carrying out the method according to the invention. A material 401 is metered via sluice 402 into shaft kiln 403. Simultaneously, heat carrier medium 414 is fed into shaft kiln 403 by conveyor 409 via sluice 410. Material 401 and the heat carrier medium 414 travel downwards in shaft kiln 403 and mix, whereby by means of the heat contained in heat carrier medium 414, material 401 is pyrolyzed at approximately 600°C.

At the lower end of shaft kiln 403, the mixture consisting of heat carrier medium 414 and pyrolysis coke 426 forming from material 401 through pyrolysis is fed onto grate 405 of brick-lined firing 407 through feeding 404. Firing 407 has starting booster 406. On grate 405, pyrolysis coke 426 burns, giving

off heat. In this way, heat carrier medium 414 is heated to approximately 1000°C. Heat carrier medium 414 consists of a coarse grained material such as sand, gravel, or split. During the firing, heat carrier medium 414 and pyrolysis coke 426 travel as far as worm 408 at the end of grate 405, by which the ash of pyrolysis coke 426 and heat carrier medium 414 are discharged. The majority of this mixture consisting of heat carrier medium 414 and ash is returned to shaft kiln 403 via conveyance 409 and sluice 410, where heat carrier medium 414 discharges the heat absorbed in firing 407 to material 401.

A small portion of the mixture consisting of ash of pyrolysis coke 426 and heat carrier medium 414 is discharged via cooling 411 and sieve 412. Through sieve 412, the ash of pyrolysis coke 426 is separated as fine material 413 from the coarser heat carrier medium 414 and heat carrier medium 414 is returned to the process. This separation is superfluous when the material to be gasified does not contain any ash-forming constituents.

The pyrolysis gas forming during the pyrolysis in shaft kiln 403 is withdrawn from the upper area of shaft kiln 403 via line 403a and fed into heat exchanger 417. Aside from water, carbon monoxide, carbon dioxide, hydrogen, and methane, the pyrolysis gas also contains higher hydrocarbons and tars as well as other organic, especially aromatic compounds as condensable components. Heat exchanger 417 is heated to a temperature of approximately 950°C by the waste gases of firing 407. At this temperature, the pyrolysis gas and the condensable substances react with steam that is contained in the pyrolysis gas. INS B3 In addition, ~~steam 416 is~~ fed into line 403a for the reactions in heat exchanger 417. To further increase the temperature in heat exchanger 417, air 415 can also be added for a partial firing of the pyrolysis gas. To improve the cracking of the accompanying tars, a catalyst can be provided in the heat exchanger.

It is also possible to add the catalyst in the flow stream to the pyrolysis gas stream and to separate it again after heat exchanger 417 and reuse it.

Heat exchanger 417 leaves a gas product whose portions of carbon monoxide and hydrogen have been maximized. This gas is fed to heat ex-

changer 421 for utilization of waste heat and into washer 422 for gas purification.

Gas product 425 is withdrawn via induced draught ventilator 423.

The waste heat from heat exchanger 421 can be used to heat the pyrolysis gas to reaction temperature for the reaction with steam.

After it has flowed through heat exchanger 417, the waste gas of firing 407 is fed through heat exchanger 418 for waste heat utilization. After gas purification 419, waste gas 424 is discharged to the surroundings via induced draught ventilator 420.

Both firing 407 and also heat exchanger 417 are operated at a pressure that only slightly deviates from atmospheric pressure and generally is somewhat less than the latter. Induced draught ventilator 423 for gas product 425 and 420 for waste gas 424 are regulated and coordinated with one another so that the pyrolysis gas is fed through heat exchanger 417 and is not sucked through the shaft oven feed into firing 407.

A ~~Embodiment example~~ EXAMPLE 1

1000 kg/h wood are gasified in the device according to Figure 4. The wood contains 3% ash (free from water) and otherwise consists essentially of 50% carbon, 6% hydrogen, 42% oxygen, and 1.9% nitrogen, calculated without water or ash. The upper caloric value is 17.9 MJ/kg in the anhydrous state. The thermal gasification efficiency is 4.97 MW. The pyrolysis is carried out at 600°C and the reaction with steam at 950°C. The working pressure is atmospheric pressure.

Gravel with a grain size from 3 mm to 15 mm is used as heat carrier medium. The gravel is heated from 600°C to 950°C. Because of the required thermal performance of 380 kW, the cycling quantity of the heat carrier medium is five times that of the wood input, that is, 5000 kg per hour. The shaft kiln is 4.5 m high and has a diameter of 1.5 m, corresponding to a fluidized bed volume of 7.5 m^3. The residence time in the shaft kiln is two hours.

In the pyrolysis, the wood is reacted so that 20 wt% of the wood remains

as wood charcoal. In the following table, the quantities and compositions of the wood and pyrolysis coke (wood charcoal) are listed:

Material flow	**Wood**	**Wood charcoal**
m [kg/h]	1000	200
H_u [MJ/kg] dry	17,9	33,5
C [wt%] daf	52,1	92,2
H [wt%] daf	4,8	2,6
O [wt%] daf	42,4	5,2
Ash [wt%] dry	3,4	17,0

The following gas product is obtained:

Caloric value [MJ/Nm^3]	10,5
H_2 [Vol.-% dry]	51,1
CO [Vol.-% dry]	39,7
CH_4 [Vol.-% dry]	0,01
CO_2 [Vol.-% dry]	9,2
H_2O [Vol.-%]	14,8
Chemical. enthalpy flow [MW]	3,9
Quantity [Nm^3/h]	1.338

The enthalpy flow of the wood charcoal in the firing is 1.86 MW. This is sufficient to generate a steam flow of 0.45 MW (360 kg/h at 950°C and atmospheric pressure) as well as to cover the heat requirement of the reaction of the pyrolysis gas with steam at the level of 0.84 MW. The firing efficiency is 85%. After accounting for the heat loss and loss through the waste gas flow, only

0.26 MW remain. With this, 324 kg/h superheated steam were generated that were relaxed via a turbine and used as heating steam. The cold gas efficiency is 79%.

INS A8

List of reference numbers:

1	Material used
2	Pretreatment step
3	Pyrolysis
4	Reaction zone
5	Pyrolysis gas
5a	Pyrolysis coke
6	Firing
7	Heat coupling
7a	Heat coupling
8	Dedusting
9	Feed water
10	Water treatment
11	Pump
12	Heat exchanger
13	Turbine
14	Fine dedusting/quenching
15	Gas product
16	Steam
16a	Waste steam
17	Heat exchanger/flue gas cleaning
18	Waste gas
19	Gas product
20	Air
101	Pyrolysis step
102	Reaction step
103	Firing
104	Wood
104a	Heat carrier medium
105	Mixture

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106 Pyrolysis gas
107 Gas product
108 Lost heat
109 Formation heat
110 Lost heat
111 Heat feed reaction step
111a Heat feed pyrolysis step
112 Superheated steam
113 Air
114 Excess heat
115 Heat loss
116 Waste gas
117 Water
118 Mixture
401 Material used
402 Sluice
403 Shaft kiln
403a Line
404 Feeding
405 Grate
406 Booster
407 Firing
408 Worm
409 Conveyor
410 Sluice
411 Cooling
412 Sieve
413 Fine material
414 Heat carrier medium
415 Air
416 Steam

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417 Heat exchanger
418 Heat exchanger
419 Gas purification
420 Induced draught ventilator
421 Heat exchanger
422 Washer
423 Induced draught ventilator
424 Waste gas
425 Gas product
426 Pyrolysis coke

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